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RAMAN SPECTRUM OF SUGAR

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Plate X

ABSTRACT. By an improved method, sugar was purified and the Raman spectrum of its solution taken. This revealed 16 Raman lines and the usual water band. The frequencies of the lines are 377*, 464*, 549*, 599*, 649, 753*, 856, 943, 1088, 1135, 1272, 1333*, 1370*, 1408*, 1472, 2865 and the water band extending from 3298—3681. The frequencies marked with asterisks have been observed for the first time. A general assignment of frequencies as due to the C—C, C—O, C—H, δ (C—H) oscillations has been made. These lines are compared with those obtained with glucose and crystalline sucrose.

INTRODUCTION

In view of the interest in the constitution of sugars from an organic or biochemical standpoint, a study of the Raman effect of this class of substances is of special importance. But it is suprising to note that very little work has been done in this direction. This is most probably due to the fact that heavy molecules of this type give rise to a strong continuous background which is found, in many cases of Raman spectra, to completely mask the lines characteristic of the molecule. The classical example of this type is glycerine—$(OH)H_2C.CH(OH)CH_2(OH)$. The continuous background in the Raman spectrum of this substance is so prominent that even with the liquid distilled in vacuum it could not be entirely eliminated. (It may incidentally be mentioned here that the author has obtained, using an improved method of distillation, an extremly good Raman spectrum for Glycerine and the results are being published.) This substance is comparatively simple when compared to heavier molecules containing a larger number of carbon atoms. Various workers have attributed this phenomenon to various causes, but with all the work done so far, the weight of evidence is that the continuum arises from an impurity and is not due to a genuine Raman scattering.

Whiting and Martin[1] were able to partly eliminate the continuous spectrum by making the solution of sucrose dust-free by precipitating with $Al(OH)_3$. They were able to record after 144 hrs. of exposure, four faint Raman lines, with frequencies 1090, 1480, 2870 and 3420 cm.$^{-1}$, the last being the water band or a superposition of this over the O-H band arising out of the O-H in sugar.

Polara [2] working with sugar solutions reported a large number of lines; the Raman frequencies of which are 625, 668, 689, 858, 945, 1037, 1134, 1224, 1339, 1425, 1488, 1683, 2016, 2055, 2113, 2164, 2404, 2718, 2813.

Kutzner [3] tried with a number of saccharides and obtained frequencies given below.

Glucose	454, 513, 1143
Galactose	1138
Fructose	1179
Maltose	1135, 1140
Saccharose	1130-1188 (broad band)

A comparison of the results obtained by Polara with those of Whiting and Martin on the one hand, and Kutzner on the other, will indicate the large discrepancies between the frequencies of the lines obtained by them. With a view to investigate the cause of these discrepancies, a study of the Raman spectrum of sugar was undertaken, the results of which are given below.

EXPERIMENTAL

While studying the Raman effect, it is important to ensure that exciting light was not decomposing the substance under investigation. N. A. Yajnik and co-workers [4] have shown that solutions of sucrose, when exposed to ultraviolet light, undergo hydrolysis even in the complete absence of acid. Hence, the solutions studied in these investigations were always tested with Fehling's solution for the abscence of reducing sugars, both before and after the exposure to the mercury arc light used as the exciting radiation. The light from the arc was condensed by a 9″ glass condenser on to the Wood's tube containing the sucrose solution. After several trials with various light filters, a combination of two filters consisting of sodium nitrite and the solution of the proper strength of Iodine in carbon tetrachloride was chosen and placed between the condenser and the scattering medium. This served to eliminate the 4047-line of the arc and beyond on the shorter wavelength region and also the continuous spectrum between 4358 Å and 4916 Å, present in the light from the mercury arc. Care was taken to run the mercury arc at a low voltage—which considerably helps to reduce the continuum. Thus the exciting source is 4358 Å which is undoubtedly the best mercury line for this work, as decomposition of sugar is avoided and the Raman lines appear between the lines 4358 Å to 4916 Å, a region free from mercury lines.

The scattered light was focussed on to the slit of the spectrograph by means of an achromatic lens. A two-prism spectrograph of high light-gathering power (which was kindly designed and constructed by the Instruments Manufacturing Section attached to the Applied Physics department) was used

to record the Raman spectrum on Ilford Isochrom plates. A comparison spectrum of copper was given on the same plate using a Hartmann's diaphram and the wavelengths determined by measuring with a Hilger comparator.

METHOD OF PURIFICATION OF SUGAR SOLUTION

A 60% solution of sucrose was prepared with redistilled water and was found to be contaminated with appreciable amounts of suspended impurities and was straw yellow in colour. Various methods of purification suggested by previous workers were tried with little success. Purification by repeated crystallisations did not appreciably improve the nature of the spectrum. Hence, a modified method of purification was adopted in this investigation. The sucrose solution was treated with the decolourising carbon-Norit A. The quantity of carbon used was about 2% of the solids in the melt and the 'wet filling' method was adopted for clear filtration. The first liquor which flowed from the filter was generally cloudy, but after fifteen or twenty minutes of running to refiltration, this cleared up. The solution was further rendered clear by centrifuging in a Sharple's super centrifuge at 5,500 r.p.m., the outflow from the centrifuge being directly collected in the Wood's tube.

RESULTS

In Plate X, figure 1 shows the Raman spectrum of sugar solution before purification with an exposure of 2 hours. Even with such a short exposure the continuous background was so strong that it was not possible to observe any Raman lines. Noting that the continuous spectrum was too strong to permit of observation of any Raman lines, attempts were made to eliminate it by purification of the solution by the method described above and by the use of suitable light filters.

Figure 2 shows the enlarged Raman spectrum of the purified solution with an exposure of 15 hours using $NaNO_2$ solution and Noviol glass as filters.

Figure 3 shows the Raman spectrum of the same solution using $NaNO_2$ and Iodine in carbon tetrachloride filters. The time of exposure in this case was 30 hours.

It is evident that in figure 3, the continuous background is least in intensity showing that this combination of filters is most efficient. The Raman lines are prominent enough to permit of the measurement of their wavelengths with a Hilger Comparator. For such of the lines which are broad and diffuse, the location of the maximum with the Comparator not being possible, a microphotometric record of the entire Raman spectrum was taken. From this record, it was easy to find both the position of such lines and their quality in respect of width and diffuseness.

The following table gives the Raman frequencies of sucrose taken as a mean of measurements made with two independant plates. The figures in parentheses indicate the relative visual estimates of the intensities.

TABLE I

Raman Frequencies of Sugar		Raman Frequencies of Glucose		
Solution I	Crystal II	Kutzner (1932) III	Wiemann (1936) IV	Author V
377*(3)	-	—	—	—
464*(3)	423	454	435 ± 25	423(3)
549*(4)br	549	513	519 ± 11	549(3)
599*(4)br	—	—	—	—
649	649	—	—	624(1)
753*	723	—	—	—
856(5)	846	—	853 ± 10	856
—	—	—	911 ± 14	919
943(3)	—	—	—	—
—	992	—	—	—
—	—	—	1020 ± 10	—
1088(10)br	1088	—	1067 ± 12	1064(7)br
1135(10)br	1135	1143	1145 ± 9	1159(10)br
1272	—	—	1200 1262 ± 8	1270
—	1300	—	—	— —
1333* 1370* 1408* (Broad diffuse band.)	—	—	1373 ± 19	1370
1472(7)sh	1463	—	1464 ± 7	1463
2865(7)br	—	—	—	2804(5)br
3298 3457 3681	—	—	—	3260

For purposes of comparison, the Raman spectrum of Glucose was also investigated. The Glucose employed was Merck's which was further purified by the method adopted for solutions of sucrose. The lines obtained with Glucose were, however, much more feeble than those for sucrose as is evident from Figure 4. Table I, column V, gives the frequencies of Glucose compared with those reported previously by other investigators.

CRYSTALLINE SUCROSE

Sugar was investigated in the solid state also. The crystal powder was contained in a triangular cell, similar to the one used by Krishnamurty [5]. Owing to the inherent difficulty in the technique involved, none of the liquid filters which are generally employed could be used and the filter made use of was the Zeiss C glass expected to transmit only the 4358-line of the mercury arc, so that the excited Raman lines originate out of this line only. A copper trough of small thickness was devised for placing between the mercury arc and the cell containing sugar crystals. Cooling water was kept in constant circulation in the trough to prevent heating and the consequent charring of the crystals. A fairly good spectrum could be obtained with 20 hours' exposure but the Raman lines were masked by the overlapping continuous spectrum and they were so faint as to be barely discernable on the enlarged print which is therefore not reproduced in the plate. Table I, column II gives the frequencies obtained for sugar in the solid state.

DISCUSSION

A reference to Table I would show that many new frequencies (noted with asterisk) have been observed in the present investigation and many points of detail, missed by previous workers, have also been recorded.

The Raman lines in solutions of sucrose may be classified as arising from the C–C, the C–O, the C–H and the δ (C–H) frequencies. Those in the region 800–950, *i.e.*, 943, 856, 753 (?), may be taken as aliphatic C–C frequencies corresponding to similar lines obtained with all aliphatics containing at least two carbon atoms. The C–O frequencies come in the region 1000–1150. In sugar the corresponding frequencies for this band are 1088, 1135. The broad and strong line at 2865 is the valence C–H frequency and the line 1472 is the δ(C–H) frequency. The lines 1333, 1370, seem to be the (C–H) deformation frequencies. But as pointed out by Koteswaram [6] the presence of a strong line at 1392 for formic acid makes this assignment uncertain. The band 3298–3681 with its intensity maximum at 3457 is well known to be due to water.

A comparison of the frequencies obtained for sugar with those for glycerine shows the close resemblance between the two and some of the other frequencies observed in sugar agree well with frequencies found in alcohols.

The following Raman frequencies of sugar bear close resemblance to those of glycerine

464, 549, 649, 856, 943, 1472

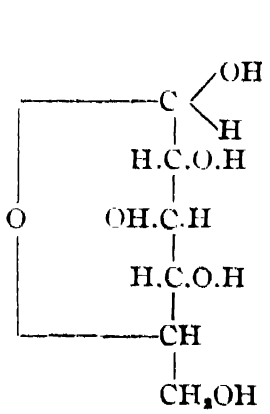
and those below compare well with the frequencies found in alcohols

1088, 1135, 1333.

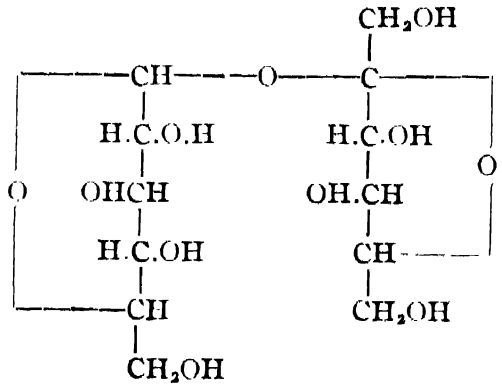
The frequency 1134 is found in the Raman spectrum of butyl and isobutyl alcohols.

Besides these, the low frequencies recorded occur in many of the aliphatic compounds and are usually attributed to the external frequencies between the different groups in these molecules.

Polara (*loc. cit.*) reported a line at 1683, which is attributed to the C=O oscillation, but the author could find no trace of any line in this region with either sucrose or glucose. This is to be expected as there is no C=O in either of the molecules as will be evident from the structural formulæ of these compounds given below :



Glucose



Sucrose

Most of the frequencies obtained by Polara between 2016 and 2718 were not noticed by the author and are highly improbable.

In conclusion, the author desires to express his grateful thanks to Dr. I. Ramakrishna Rao for his helpful guidance throughout the progress of this investigation.

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PLATE X

Fig. 1

Fig. 2

Fig. 4

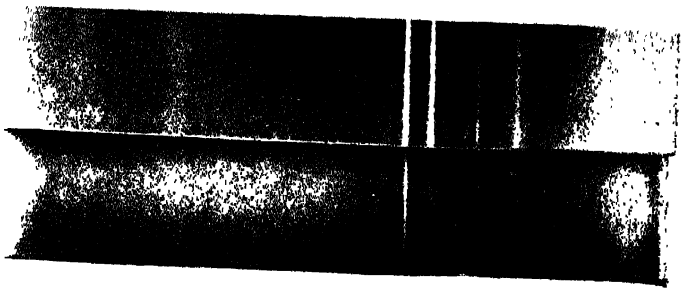

Fig. 3